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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

New polymer electrolytes were prepared and studied by complex impedance spectroscopy, pulsed field gradient, and MAS NMR. A new class of polymeric mixed ionic-electronic conductors was also prepared and studied.

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OFFICE OF NAVAL RESEARCH

FINAL REPORT

for

Contract N00014-80-C-0532

Technical Report No. 21

Basic Studies of Polymer Electrolytes Suitable for Advanced Electrochemical Devices

by

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August, 1988

Research Accomplishments

As we have described in previous end-of-year reports, we have made advances in several areas of polymer electrolytes, only the highlights are listed here.

(i) Experiments on the polyethylene oxide $NaBF_4$ complex doped with varying amounts of $NaBH_4$ strongly indicate that the cations are not transported down helical tunnels as originally proposed.

(ii) A new class of polyphosphazene comb polymers was synthesized (eg. $[NP(OC_2H_4OC_2H_4OCH_3)_2]_n$) and the salt complexes were well characterized. For many years these polymer salt complexes displayed the highest ionic conductivity of any solvent-free polymer electrolyte.

(iii) Pulsed field gradient NMR studies of polymer electrolytes were performed to determine diffusion coefficients for Li^+ (^{7}Li NMR) and $SO_3CF_3^-$ (^{19}FNMR). These represent some of the most precise and extensive data or diffusion coefficients in polymer electrolytes, and they provide insight into ion pairing in these materials.

(iv) A new class of mixed ionic-electronic conductors was synthesized and investigated. These consist of a polar polymer complexed with NaI_x. When x = 1, the material is a simple ionic conductor. As x increases, electronic conductivity is observed and eventually at large values of x electronic conductivity dominates. In the intermediate range, both ionic conductivity and electronic conductivity increase with increasing x. We hope to continue studies of this correlation between ionic and electronic conductivity, and the mechanism for electronic conductivity.

(v) We prepared the first solvent-free polyelectrolytes with good ionic conductivity. Initially these were plasticized materials but more recently, phosphazene comb polymers have been synthesized and studied. The latter include new anion conductors that have higher conductivities than any previously reported.

Listing of Technical Reports and Journal Articles

Report No.	Title and Authors
001	"Transference Number Measurements for the Polymer Electrolyte Poly(ethylene oxide)•Na SCN", R. Dupon, D. H. Whitmore and D. F. Shriver, J. Electrochem. Soc., 128, 715 (1981).
002	"Structure and Ion Transport in Polymer Salt Complexes", D. F. Shriver, B. L. Papke, M. A. Ratner, R. Dupon, T. Wong and M. Brodwin, Solid State Ionics, 5, 83-88 (1981).
003	"Ion Pairing in Polyether Solid Electrolytes and its Influence on Ion Transport", B. L. Papke, R. Dupon, M. A. Ratner and D. F. Shriver, Solid State Ionics, 5, 685-88 (1981).
004	"Mechanism of Ionic Conduction in Alkali Metal-Polymer Complexes", D. F. Shriver Matthew Stainer, and R. Dupon, Journal of Power Sources, 9, 383-88 (1983).
005	"The Influence of Ion Pairing on Cation Transport in the Polymer Electrolytes formed by Poly(ethylene oxide) with Sodium Tetrafluoroborate and Sodium Tetrahydroborate", R. Dupon, B. L. Papke, M. A. Ratner, D. H. Whitmore and D. F. Shriver, J. Am. Chem. Soc., 104, 6247 (1982).
006	"Ion Transport in the Polymer Electrolytes formed between Poly(ethylene succinate) and Lithium Tetrafluoroborate", R. Dupon, B. L. Papke, M. A. Ratner and D. F. Shriver, J. Electrochem. Soc., 131, 3, (1984).
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009 "Polyphosphazene Solid Electrolytes", P. M. Blonsky, P. Austin, H. R. Allcock and D. F. Shriver, J. Am. Chem. Soc., 106, 6854 (1984).

010 "Preparation and Electrical Response of Solid Polymer Electrolytes with Only One Mobile Species", L. Charles Hardy and D. F. Shriver, J. Am. Chem. Soc., 107, 3823 (1985).

011 "Polyphosphazenes with Etheric Side Groups: Prospective Biomedical and Solid Electrolyte Polymers", H. R. Allcock, P. E. Austin, T. X. Neenan, J. T. Sisko, P. M. Blonsky and D. F. Shriver, Macromolecules, 19, 1508 (1986).

012 "Complex Formation and Ionic Conductivity of Polyphosphazene Solid Electrolytes", P. M. Blonsky, D. F. Shriver, P. Austin and H. R. Allcock, Solid State Ionics, 18 & 19, 258-64 (1986).

013 "Increased Dimensional Stability in Ionically Conducting Polyphosphazenes Systems", D. F. Shriver and J. S. Tonge, J. Electrochem. Soc., 134, 269 (1987).

014 "Ionic Conductivity in Branched Polyethylenimime-Sodium Trifluoromethanefulfonate Complexes. Comparisons to Analogous Complexes made with Linear Polyethylenimine", C. S. Harris, M. A. Ratner and D. F. Shriver, Macromolecules, 20, 1778 (1987).

015 "Synthesis, NMR Characterization and Electrical Properties of Siloxane-Based Polymer Electrolytes", R. Spindler and D. F. Shriver, Macromolecules, 21, 648 (1988).

016 "Effect of Sidechain Length and Crosslinking on Ionic Conductivity", J. S. Tonge, P. L. Blonsky, D. F. Shriver, H. R. Allcock, P. A. Austin, T. X. Neenan and J. T. Sisko, submitted to Electrochem. Society.

017 "Ion Transport in Solvent-Free Polymers", D. F. Shriver and M. A. Ratner, Chem. Rev., 88, 109 (1988).

018 "Solvent Free Polymer Electrolytes", J. S. Tonge and D. F. Shriver, Polymers in Electronics, in press.

019 "Polymeric Electrolytes", P. M. Blonsky, S. Clancy, L. C. Hardy, C. S. Harris, R. Spindler, J. S. Tonge and D. F. Shriver, ChemTech, Vol. 17, No. 22, 758 (1987).

020 "A New Class of Cation Conductors: Polyphosphazene Sulfonates", S. Ganapathiappan and D. F. Shriver, Macromolecules, 21, 2299 (1988).

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